

Calcium Production by the Electrolysis of Molten CaCl_2 —Part I. Interaction of Calcium and Copper-Calcium Alloy with Electrolyte

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This paper describes the interaction between calcium and molten CaCl_2 and the solubility of calcium in this melt, depending on the calcium content in the copper-calcium alloy that comes in contact with the molten CaCl_2 . The negative influence of the dissolved calcium on the current efficiency was verified. The negative effects of moisture and CaO impurities on the calcium current efficiency were demonstrated. The dependence of the current efficiency and the purity of the metal obtained by the electrolysis conditions were studied in a laboratory electrolyzer (20 to 80 A).

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I. INTRODUCTION

NUMEROUS efforts to produce calcium by the electrolysis of CaCl_2 have been made since the mid-nineteenth century; however, none of them has provided satisfactory results, primarily due to the high calcium solubility in molten CaCl_2 .

The first successful experiments were performed in Germany (1904) and the USA (1905). Calcium ingots in the form of rods were obtained at a cooled touching cathode that was slowly lifted from the melt.^[1,2] The process was performed at a high cathode current density (not lower than 30 to 60 A cm^{-2}) and a cell voltage of 25 to 30 V. The main disadvantages of the method were the low calcium current efficiency (40 to 50 pct) and the high consumption of materials and electric energy. Moreover, the calcium produced contained many impurities and required subsequent distillation.

Investigations aimed at the development of calcium production by electrolysis of its oxide dissolved in the CaCl_2 melt and eutectic CaCl_2 - CaF_2 mixture^[2] and by the electrolysis of molten CaF_2 with a graphite anode at 1723 K (1450 °C)^[3] have not been successful. Paper^[4] demonstrates the possibility of producing calcium by the electrolysis of a $\text{Ca}(\text{NO}_3)_2$ - KNO_3 mixture at 453 K to 473 K (180 °C to 200 °C) with a cathode current density of 0.03 to 0.12 A cm^{-2} . This method is not industrially competitive because of the low cathode process velocity and the oxidation of the spongy calcium cathode deposit when it is separated from the salt by hydrometallurgical and pyrometallurgical methods.

The process of calcium production, which has existed in Russia since 1949, comprises two independent technological stages: (1) calcium extraction by the electrolysis of a CaCl_2 - KCl (15 to 20 wt pct) melt at a copper-calcium alloy (Cu-Ca alloy) cathode at 923 K to 988 K (650 °C to 715 °C) and (2) calcium separation from the calcium-rich alloy by vacuum distillation.^[1] The second stage is conducted in an apparatus of intermittent operation and is considered to be the weakest point. The distillation conducted using the existing equipment does not meet the modern ecological requirements claimed by newer technologies and demonstrates low technical-economic data.

Metallothermically, calcium is reduced from its oxide in vacuum by metal powder (aluminum and silicon) at 1373 K to 1473 K (1100 °C to 1200 °C). Comparative parameters, advantages and disadvantages of the existing industrial methods of calcium are presented in Reference 5. Both methods are accompanied by considerable energy consumption and relatively low yields of calcium due to the energy expended during the first stage (70 to 80 and 60 to 65 pct, respectively^[5]). Therefore, the improvement of existing technologies and the development of new methods of pure calcium production are needed.

We developed a method of electrochemical calcium production from molten CaCl_2 that allows for a continuous process. Its essence lies in the development of a two-section electrolyzer. In the first section, the Cu-Ca alloy is enriched with calcium formed during the electrolysis of a CaCl_2 - KCl electrolyte. In the second section, the Cu-Ca alloy is used as the anode, and pure calcium is extracted from the molten CaCl_2 at the inert iron cathode as a final product.

The purpose of this paper is to describe the processes occurring at the electrodes and in the electrolyte within both sections of the electrolytic cell, as well as the electrolysis technological parameters. The following paper suggests the optimal construction of electrolyzers

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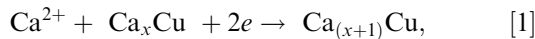
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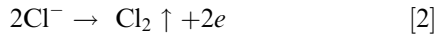
to produce the Cu-Ca alloy as a soluble anode, from which calcium is obtained at the cathode.

A. Calcium Solubility in Molten CaCl_2 and Its Influence on the Decrease in Current Efficiency

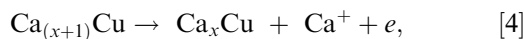
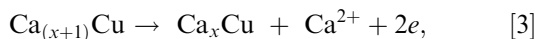
The main electrode reactions in the first section of the electrolyzer are the discharge of calcium cations at the Cu-Ca alloy cathode, which leads to calcium enrichment:



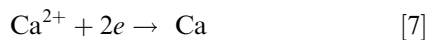
and the discharge of chlorine anions at the graphite anode and gaseous chlorine immersion:



Electrochemical reactions of the calcium anode dissolution from the Cu-Ca alloy:



and calcium cathode deposition at the inert (iron) and then at the proper substrate occur in the second section:



A side reaction of the reverse calcium solubility from the cathode to the molten salt decreases the current efficiency during the electrolysis. To solve this problem, we needed to determine the mechanism of metal dissolution in the molten salt and the form that the metal acquires in the molten salt. Reviews^[6,7] and a paper^[8] represent historical aspects of the disputes on this issue. Based on the studies of the molten CaCl_2 -Ca solutions by physical-chemical and electrochemical methods, the majority of the researchers agreed that when calcium is dissolved in the proper salt, calcium subcations (Ca^+) are formed according to the recharge reaction:



This equilibrium shifts right as the temperature increases.

To establish the electrolysis technology, it is important to understand that Reaction [8] causes weight losses of the deposited cathode calcium, decreasing the calcium current efficiency. These losses can be reduced by the cathode deposition of calcium on the Cu-Ca alloy. Data represented in paper^[8] demonstrate that as the calcium activity decreases from 1 (pure calcium) to 0.01 (the Cu-Ca alloy containing 30 at.pct of calcium), the

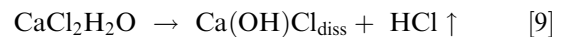
calcium solubility (equilibrium concentration, mol pct) in the CaCl_2 melt decreases 8.2 times at 1123 K (850 °C).

This explains why the Cu-Ca alloy, and not pure calcium, is used as the cathode during the electrolysis to decrease calcium losses. The alloy functions as a weighing material for calcium, as pure calcium is less dense than the CaCl_2 and CaCl_2 -KCl melts and, hence, floats to the surface of the melt where it can be oxidized by the surrounding oxygen, which is one more potential source of loss for the target product.

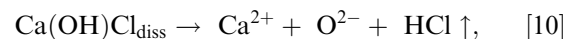
There is an analogous influence on the decrease in calcium solubility in the molten salt in CaCl_2 dilutions with another salt (for example KCl), which does not interact with calcium, as well as a lowering of the molten salt temperature to the minimal possible values.

B. Influence of Impurities in the Electrolyte on the Current Efficiency

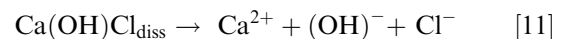
The presence of impurities in the electrolyte negatively influences the calcium current efficiency. Dissolved calcium hydrochloride $\text{Ca}(\text{OH})\text{Cl}$ is the most detrimental impurity and is formed while melting poorly dried CaCl_2 .^[9-11]



As the temperature is increased, the impurity is partially decomposed, forming dissolved calcium oxide and gaseous hydrogen chloride:

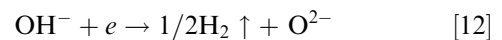


and the remaining portion dissociates:

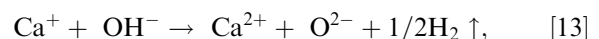


The hydroxide anions can exist as impurities in molten salts at temperatures above 1173 K (800 °C).

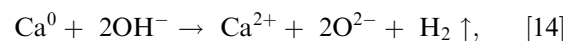
That is why constant current is wasted to clean the electrolyte from the hydroxide anions, which can discharge at the cathode, during the initial electrolysis period in both sections of the electrolyzer:



Calcium is extracted at the cathode only after the electrochemical purification of the electrolyte. Since the consumable component, CaCl_2 , has to be regularly added to the electrolyte during the first section of the electrolytic cell, Reactions [9] through [11] occur if there is residual moisture present and are followed by chemical reactions in the electrolyte with dissolved calcium subcations:



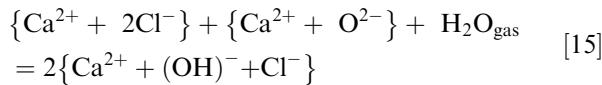
and metallic calcium according to the reaction



storing oxygen anions in the electrolyte.

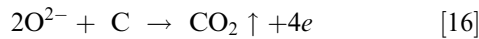
Electrochemical decomposition of the hydroxide anion at the cathode according to Reaction [12] and highly undesirable hydrogen penetration into the cathode calcium or its alloy may occur in parallel.

One more fact that has a negative influence on the calcium current efficiency is the presence of dissociated calcium oxide, which is formed according to Reactions [10], [13], and [14], and according to References 9 through 11, the presence of moisture in the gas phase of the cell favors the formation of Ca(OH)Cl:



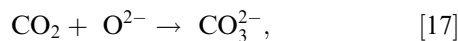
Thus, Reactions [12] through [14] result in the losses of the current and target product and, hence, the decrease in the current efficiency.

The presence of oxygen anions in the electrolyte of the first section of the electrolyzer leads to increased consumption of the graphite anode because of its oxidation:

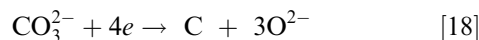


This results in carbon dispersion within the electrolyte according to the following reactions:

a portion of the CO₂ from Reaction [16] dissolves in the anolyte and unites with the oxygen anions, forming carbonate anions:



which are transferred by the electrolyte flow to the cathode, where they are discharged, forming the carbon dispersion in the electrolyte:

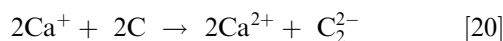


The oxygen anions are further transferred to the anode and again undergo Reaction [16], closing the transport-electrochemical cycle with wasted current consumption. The electrolyte is purified from the disperse carbon in two ways. First: carbon particles in the anolyte react with dissolved CO₂ and form removable gaseous CO.

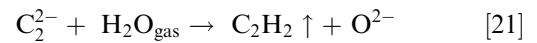


Since the CO₂ solubility in the molten CaCl₂ is small, the electrolyte purification from the disperse carbon according to Reaction [19] is slow.

The second way: a portion of the disperse carbon reacts with dissolved Ca and carbide anions are formed.



Their concentration in the electrolyte is at the 0.1 to 0.5 pct level.^[9] At the interface of the electrolyte/gas, the carbide anions can interact with air moisture and extract ethyne



It follows that purification from the air components, primarily from moisture and CO₂, is needed both for the electrolyte and the gaseous medium of the cell.

The second section of the electrolyzer does not have a graphite anode, which is why its electrolyte is not purified from the oxygen anions. The CaO solubility in molten CaCl₂ is uniquely high; at 1123 K (850 °C) it is 21.0 mol pct (11.84 wt pct).^[12] Therefore, CaO dispersion at low concentrations is unlikely. The Cu-Ca alloy anode passivation by the solid 2CaO·CuO double oxide layer at high anode current density results in an increasing electrolyzer voltage drop and can have a negative impact.

For this reason, it is especially important to purify CaCl₂ from the residual moisture for the second section of the electrolytic cell. The process of calcium production should be performed in hermetic electrolyzers to eliminate chemically active air components (O₂, H₂O, and CO₂).

II. EXPERIMENTAL

In the second section of the electrolyzer, the calcium extraction from the Cu-Ca alloy, the anode part of the bipolar electrode, proceeds according to anode Reactions [3] and [4] and cathode Reactions [5] through [7].

The high chemical activity of the Ca-CaCl₂ and Ca-Cu-CaCl₂ molten systems and the high exchange currents at the electrodes made of calcium and Cu-Ca alloys did not allow the use of conventional methods to study the electrode processes, as all known ceramic materials are reduced by calcium and, therefore, cannot be used to build cells.

Preliminary experiments on calcium production from its alloys with copper demonstrated that ring-like moving flows are formed in the liquid cathode metal as a result of the electromagnetic forces appearing at the current flow. Consequently, the stability of the liquid cathode form depends on its size (square) and the current. If the electrolysis current exceeds 20 to 30 A, a “pool” of liquid calcium up to 30 mm in diameter can be maintained. This effect was used to develop a technique for analysis of the electrode process. Experiments on the anode and cathode current efficiencies were performed in the electrolyzer; the principal scheme is presented in Figure 1. The bath (Ø120 mm, height 200 mm, 2000 cm³) and the cathode rod were made of the low-carbon steel, which is inert to calcium and its alloys with copper. The electrolyte made of pure CaCl₂ was preliminary dehydrated at 573 K (300 °C) in a vacuum for 6 hours, and then it was treated with chlorine and hydrogen chloride to eliminate oxides. The oxide concentration in molten CaCl₂ after the treatment did not exceed 0.2 wt pct. The amount of the loaded electrolyte was 800 to 1000 g.

The preliminary Cu-Ca alloy purified from the oxides was loaded through the gateway. The weight of the alloy

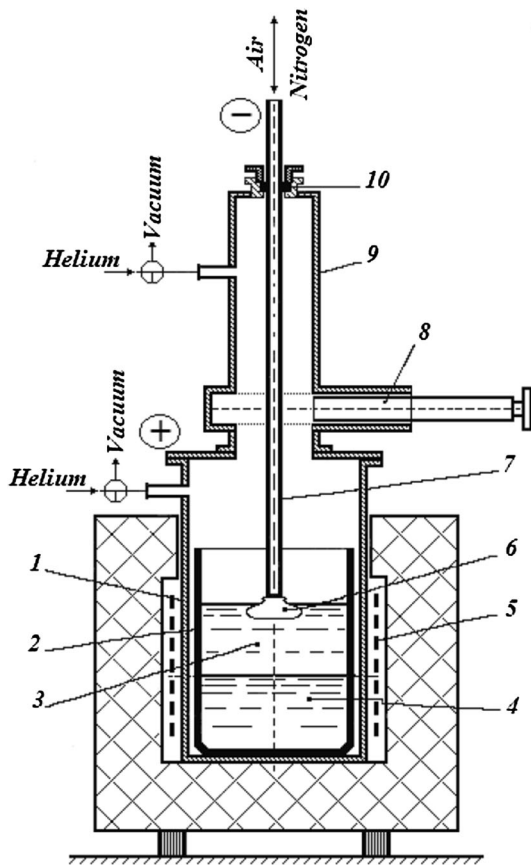


Fig. 1—Laboratory electrolyzer for calcium production. 1: case; 2: steel container (anode current lead); 3: electrolyte; 4: Cu-Ca alloy; 5: heaters; 6: liquid calcium; 7: cathode; 8: damper; 9: gateway chamber; and 10: gland seal.

was calculated so that the calcium concentration change did not exceed 2 to 3 wt pct during each current efficiency measurement and hence, did not influence the experimental results. All experiments were conducted with liquid Cu-Ca alloys according to the phase diagram.^[13,14]

During the experiment, the probes of the electrolyte, alloy, and metal were used for the analysis. The current value was from 20 to 80 A, depending on the desired current densities.

The electrolysis was performed as follows: when the desired temperature was reached, the electrolyte was left in contact with the loaded alloy for 2 to 3 hours to achieve near-equilibrium conditions. Based on the results of the chemical analysis of samples of the melt and the Cu-Ca alloy in contact with each other, such a condition continues for a few minutes. The melt was further immersed 3 to 5 mm deep in the cathode, and the current was switched on; calcium metal extraction at the cathode could be observed through the viewing window. After the desired amount of electricity passed, the obtained calcium was frozen by nitrogen bubbling through the hollow cathode and was removed through the gateway. Figure 2 demonstrates one of the calcium deposits extracted from the electrolytic cell. The experiments were performed under dried helium and argon



Fig. 2—Calcium deposit.

atmospheres. The temperature in the electrolyzer was regulated by a thermoregulator with an accuracy of ± 2 °C.

The cathode and anode current efficiencies were determined by the weight increase and decrease, respectively.

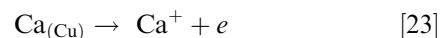
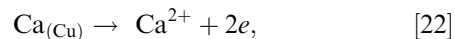
The compositions of the melt, anode alloy, and cathode deposit were determined by the spectral emission method with an iCAP 6300 Duo inductively coupled plasma optical emission spectrometer (Thermo scientific).

III. RESULTS AND DISCUSSION

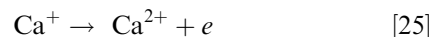
A. Anode Current Density

Tests on the anode and cathode current efficiencies were performed without separation of the electrode media, which resulted in the cross impact of the electrode processes, especially at low current densities.

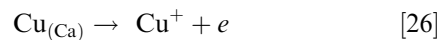
The anode dissolution of the Cu-Ca alloy can be accompanied with several reactions that define the calcium current efficiency:



Additionally, side reactions can occur:



According to Reference 8, the dissolution mechanisms of pure calcium and calcium from the Cu-Ca alloy in molten CaCl_2 are the same. At high anode current densities and low calcium concentration in the surface alloy layer, copper ionization cannot be neglected:



The fraction of Reaction [26] will be minor due to the large difference in the standard copper and calcium

potentials; however, since copper is a contaminant in calcium, the occurrence of Reaction [26] should be considered.

Observations on the anode polarization of the Cu-Ca alloy suggested that the overcharge current densities corresponding to Reactions [23] and [25] can reach 0.5 A cm^{-2} .

Experiments performed at low anode current densities demonstrated that the anode current efficiency during the ionization of the alloy, which contained 45 wt pct of calcium for two-electron process, varied from 112 to 135 pct [the anode current density was 0.3 A cm^{-2} at 1128 K (855 °C)], which suggests that a large proportion of Reactions [23] and [24] occurred which result in calcium subcation formation.

Wide scatter in the results of the anode current efficiency determination was observed. Therefore, we limited ourselves to investigating the current density at an interval of 1 to 2 A cm^{-2} , where it was possible to obtain reproducible data. At anode current densities over 2 A cm^{-2} , copper appeared in the cathode deposit, and its concentration exceeded 7×10^{-3} wt pct.

Figure 3 shows the results of the anode calcium current efficiency detection at different calcium concentrations in the melt. The maximum concentration (62 to 65 wt pct calcium) was defined by the alloy density sufficient to keep it in the electrolyte bulk during the electrolysis; the minimal concentration (30 to 35 wt pct of calcium) is defined by the liquidus temperature, which maintains the alloy in a liquid state. Cu-Ca alloys of the same concentration interval are used in industrial cells.

The major changes in the calcium current efficiency are due to its concentration in the alloy, and there is a relatively small influence of the current density, especially during the ionization of calcium-rich alloys, which agrees with the results of the calcium activity detection in the alloy.^[15]

The set values will change as the electrolyzer size and current load change, but due to the better hydrodynamic characteristics of the molten salt, the current efficiency increases and the permissible calcium concentration in the alloy should decrease. Common regularities of the anode dissolution of the Cu-Ca alloy should remain unchanged.

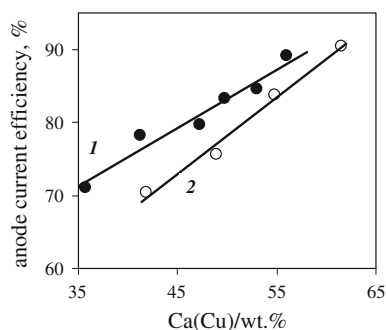


Fig. 3—Dependence of the calcium anode current efficiency on the calcium concentration in the Cu-Ca alloy and anode current density (A cm^{-2}) at 1133 K (860 °C): 1—1; 2—2.

B. Cathode Current Efficiency

The current density and electrolysis temperature are believed to impose a significant influence on the cathode current efficiency. This follows from the experimental results of the interaction of calcium and its alloy with molten CaCl_2 .

The metal deposition is accompanied by the discharge Reactions [5] through [7] and side Reaction [8].

When the process is set, Reactions [6] and [7] take place simultaneously. The fraction of each reaction is defined by the polarization current density. The impact of Reactions [5] and [8] increases with increasing temperature and decreases with increasing polarization current density.

A specific fraction of the calcium subcations, which are formed by Reactions [5] and [8] due to diffusion and convection, are transported to the anode and are oxidized. This leads to a decrease in the current efficiency on the anode and on the cathode. Moreover, this effect is more significant at larger potential differences between the electrodes and at the higher temperatures. In contrast to the anode, whose surface area was constant, the real cathode area increased during the electrolysis. That is why the values of the cathode current density were calculated by the ratio of the current value and the initial surface area of the cathode bar immersed in the electrolyte. When the amounts of the current passed were equal, the sizes of the frozen calcium ingots were constant.

Figure 4 demonstrates that the maximum cathode current efficiency is observed in the region of 4 to 6 A cm^{-2} . As was expected, the current efficiency increased due to a relative decrease of the fraction of Reaction [7]. The decrease in the current efficiencies at high current densities is explained by the electrolyte overheating in the near-cathode layer, which increases both the calcium solubility and convective flows that transfer calcium subcations to the anode where they are oxidized. An analogous effect was observed when the current efficiency dependence on temperature was studied (Figure 5).

The studies demonstrated that the anode current efficiency has a great influence on the cathode calcium current efficiency. Figure 6 shows the electrolysis results performed at an anode containing 58 wt pct calcium at a

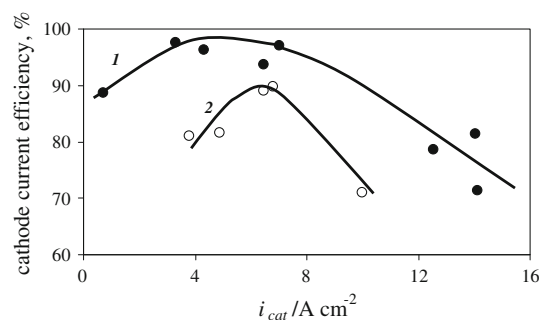


Fig. 4—Dependence of the calcium cathode current efficiency on the cathode current density and calcium concentration in the Cu-Ca alloy (wt pct) at 1133 K (860 °C): 1—(58 to 60); 2—(35 to 42).

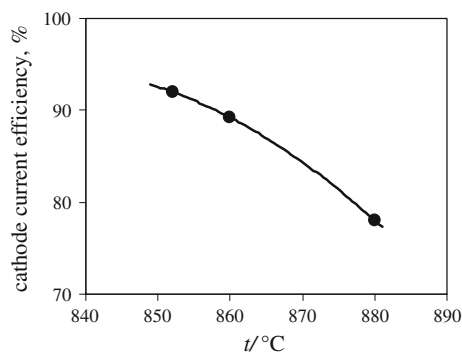


Fig. 5—Temperature dependence of the calcium cathode current efficiency at a current density of 6 A cm^{-2} and 56 wt pct calcium in the Cu-Ca alloy.

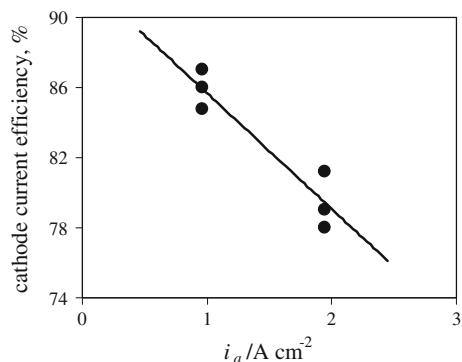


Fig. 6—Dependence of the calcium cathode current efficiency on the anode current density: 58 wt pct calcium in the alloy, $t = 1133 \text{ K}$ (860°C), $i_{\text{cat}} = 5 \text{ A cm}^{-2}$.

constant cathode current density of 5 A cm^{-2} . As the current density increases from 1 to 2 A cm^{-2} , the calcium current efficiency decreases by 10 pct due to the increased current fraction of Reaction [8]. Analogous results were obtained for the alloys containing 40 wt pct calcium.

A noticeable decrease in the calcium current efficiency was observed in the melt containing calcium oxide (see Figure 7), which, based on the results of the calcium and $\text{CaCl}_2\text{-CaO}$ melt interactions, could be predicted. The increase in the calcium subcation fraction inevitably leads to side reactions, which influence the cathode process that is observed at electrolysis.

The selection of the electrode process parameters defines the impurities concentration, primarily the copper concentration. Despite the significant difference in the standard electrode potentials of calcium and copper, the danger of copper contamination of calcium cannot be neglected, especially at high densities and low calcium concentrations in the alloy.

Experimental results, which demonstrate the dependence of the copper concentration in the calcium cathode on the anode current density and anode alloy composition, are presented in Table I. The experiments were performed at 1128 K (855°C) and a cathode current density of 5 A cm^{-2} .

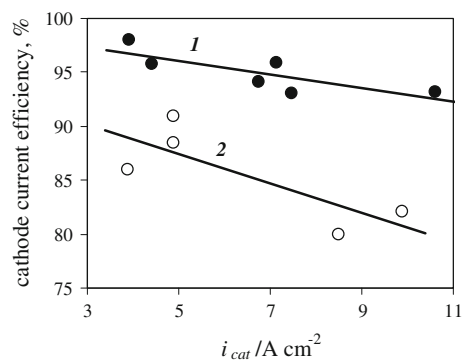


Fig. 7—Dependence of the calcium cathode current efficiency on the cathode current density at 1133 K (860°C) in electrolytes (56 wt pct of calcium in the Cu-Ca alloy): 1—without CaO; 2—with 3 wt pct CaO.

Table I. Dependence of the Copper Concentration in the Cathode Calcium on the Anode Current Density and Anode Alloy Composition

i_a (A cm^{-2})	Cu in the Anode (Weight Percentage)	Cu in the Cathode (Weight Percentage $\times 10^3$)
1.0	40	5.6
	45	6.2
	51	9.3
	58	15
	65	68
2.0	40	5.7
	45	6.5
	46	14
	52	11
	58	12

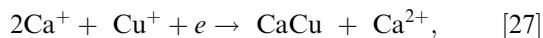
Under our experimental conditions, the minimal copper concentration in the cathode calcium can be obtained only if calcium-rich alloys are used and the anode current density does not exceed 2 A cm^{-2} .

The results for the copper concentration were obtained in a bath with good thermostatic control that nearly eliminates alloy mixing. The same can be referred to the small influence of the electromagnetic field that mixes the alloy at current loads not exceeding 80 A. In larger electrolyzers, where the bath is non-isothermal and magnetic fields have a great influence, the limiting allowable current density values can be significantly higher, even at lower calcium concentrations in the alloy.

Undesirable copper transfer from the anode to the calcium cathode can occur in several ways.

One way is the direct reduction of copper subcations (Cu^+) that were formed at the anode alloy, according to Reaction [26], and reached the cathode. This reduction at the calcium cathode is highly improbable, as there is a reducing agent in the form of delocalized electrons of Reaction [8] in the electrolyte.

The second way is more probable; it produces a copper subcation reduction by delocalized electrons and calcium subcations in the electrolyte bulk, with the formation of the nano-sized particles of the alloy



which are transferred by convective flows to the surface of the liquid calcium cathode, where the cathode consumes them.

The third way is the anode alloy dispersing in the electrolyte in the form of micro- and nano-drops of the alloy and their transfer by the convective flows from the anode to the cathode. The absorbance by the cathode calcium is possible only at large electrolysis currents.

The copper concentration in calcium is influenced by other factors. We have experimentally established that when the Cu-Ca alloy is used during electrolysis, the cathode calcium is contaminated by copper to a greater extent. This is one more point that proves the necessity of the complete isolation from the electrolyzer gaseous phase of active oxygen components (relative to the metal calcium and electrolyte). Otherwise, it is impossible to produce pure metal calcium with an acceptable current efficiency.

The results were used to develop the technique of calcium refining from its alloy.^[6]

IV. CONCLUSIONS

The primary and side electrode and chemical processes during the electrolysis of molten CaCl_2 containing dissolved calcium and impurities were described.

The influence of the conditions of electrolysis (the copper content in the copper-calcium alloy anode, the anode and cathode current density, and temperature) on the value of the cathode and the anode current efficiencies was investigated in a hermetic laboratory electrolyzer with an amperage up to 80 A.

The optimal parameters of calcium extraction from copper-calcium alloy by the electrolysis of molten CaCl_2

in a semi-industrial electrolyzer with an amperage of 0.5 to 3.0 kA were obtained for further investigation.

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